



## Supported Ir–Pd nanoalloys: Size–composition correlation and consequences on tetralin hydroconversion properties

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### ABSTRACT

A series of Ir–Pd/SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> catalysts has been prepared by incipient wetness co-impregnation of acetylacetonate precursors and treated by reductive thermal decomposition. The decomposition has been followed by combined thermogravimetry, differential thermal analysis, and mass spectrometry, showing a marked difference between the bimetallic and monometallic cases. The catalysts characterization by transmission electron microscopy and single-nanoparticle energy dispersive X-ray spectroscopy reveals that the particles are bimetallic and exhibit a size–composition correlation. More generally, the enrichment of larger particles with the less cohesive element (Pd in the present case) *via* Ostwald ripening is here claimed to be inherent to the thermal activation treatments used in the preparation of bimetallic catalysts. The catalysts have been tested in the hydroconversion of tetralin, which is considered as a model molecule for gas oil upgrading by selective ring opening. At 350 °C, 4 MPa H<sub>2</sub>, and in the presence of ppm amounts of H<sub>2</sub>S, hydrogenation, dehydrogenation, and ring-opening/contraction products (ROCPs) are formed. While the activity increases with the Pd content, the selectivity to ROCPs reaches a maximum for the Ir<sub>55</sub>–Pd<sub>45</sub> composition and increases with the sulfur concentration. The structural and catalytic results are combined to propose a qualitative model relying on metal–acid bifunctionality and size–composition correlation. While the particle size drives the number of surface sites, the corresponding surface composition governs the hydrogenation efficiency of these sites. Therefore, by controlling the mean metal composition of the catalyst, it is possible to tune the activity–selectivity balance.

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### 1. Introduction

Going further than aromatics saturation, the selective ring opening of polyaromatic hydrocarbons is a promising route to improve the combustion properties of diesel fuels and consequently reduce undesirable emissions [1]. In order to increase significantly the cetane number, unselective cracking and branching isomerization must be avoided [2]. Ideally, linear paraffins could be formed by the selective opening of all rings. In addition, due to the presence of residual sulfur in pre-hydrotreated fuels, the catalysts must be thioresistant.

Most of researches on selective ring opening have used metal–acid bifunctional catalysts. The role of the metal function is to activate hydrogen for hydrogenation–dehydrogenation steps and possibly favor selective hydrogenolysis of the rings. Hydrogenolysis is known to be catalyzed by noble metals such as Ru, Rh, and Ir. The pioneering work of McVicker et al. has shown the ability of Ir to promote hydrogenolysis of C<sub>6</sub> rings [3]. However, even on Ir, C<sub>6</sub> ring opening is much slower than C<sub>5</sub> ring opening. Thus, the de-

sired role of the acid function is to favor contraction of C<sub>6</sub> rings *via* isomerization on Brønsted acid sites, prior to ring opening. Nevertheless, the catalyst acidity should be mild enough to prevent cracking and secondary isomerization. Moreover, through electron transfer, the support acidity provides thioresistance to the metal nanoparticles [1].

The current strategies in selective ring opening consist in the use of microporous or mesoporous acidic materials loaded with noble metals. However, as a conclusion of several studies using decalin, tetralin, or naphthalene as model molecules [3–17], it remains challenging to obtain both a resistance to poisoning by sulfur, and a high selectivity ratio between C<sub>10</sub> ring-opening products and C<sub><10</sub> cracking products. Moreover, along with ring-opening products, a large proportion of decalin skeletal isomers (or “ring-contraction products”) is generally formed. Although less desirable than ring-opening products in terms of cetane number, such compounds could be important intermediates to ring-opening steps in real feedstocks. Indeed, using bifunctional catalysts, several works have obtained significant cetane number enhancements for pre-hydrotreated light cycle oil feedstocks [10,13,18].

We have recently shown that Ir supported on amorphous silica–alumina (ASA) is thioresistant and active in tetralin hydrogenation,

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ring contraction, and ring opening [16,19]. The selectivity to ring-opening/contraction products (ROCPs) is roughly proportional to the acid/metal site number ratio. Thus, a low-loaded (<1 wt.%) Ir catalyst supported on an acidic ASA (40 wt.% silica in our case) was found to be an optimal combination in terms of selectivity to ROCPs (>50%) and cracking products (<10%). However, the selectivity to ring-opening products remained low (<10%) [16].

Palladium exhibits excellent properties in terms of hydrogen activation and thioreistance [20]. In an attempt to further improve the catalytic performances of our ASA-supported system, we have investigated the structural and catalytic properties of Ir–Pd/ASA bimetallic catalysts obtained by co-impregnation of ASA with acetylacetonates. Transition-metal acetylacetonates have proven to be efficient precursors to prepare contaminant-free supported catalysts with a high degree of metal dispersion and thermal stability [21]. However, unlike for other Pd-based bimetallic systems [22] such as Cu–Pd [23,24], Mn–Pd [25], Pt–Pd [26], Ni–Pd [27,28], and Co–Pd [29], the synthesis of Ir–Pd catalysts by combining acetylacetonates has never been attempted to our knowledge. In the bulk phase, similar to that of Ir–Pt, the phase diagram of Ir–Pd presents a miscibility gap below 1500 °C at 50 at.% composition and ranging from ca. 11 to 98 at.% Pd at 500 °C [30]. This may increase the difficulty to obtain Ir–Pd nanoalloys with respect to the above-mentioned Pd-based ones.

Besides, few catalytic studies have been devoted to the Ir–Pd system. Recently, Persson et al. synthesized a number of Pd-based bimetallic catalysts for methane combustion. Ir–Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was prepared by impregnation using IrCl<sub>3</sub> and Pd(NO<sub>3</sub>)<sub>2</sub> precursors, but separate particles were obtained [31]. López-De Jesús et al. prepared Ir–Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts from IrCl<sub>3</sub> and PdCl<sub>2</sub> for liquid-phase hydrogenation of benzonitrile and evidenced a nanoparticle size–composition correlation [32]. Using a colloidal method, Shen et al. synthesized Ir–Pd/C catalysts and observed a positive effect of Ir addition to Pd for ethanol oxidation in alkaline media [33]. Similarly to our study, Rocha et al. investigated tetralin hydroconversion over a dealuminated HY zeolite loaded with Ir–Pd particles, which were obtained from (NH<sub>4</sub>)<sub>3</sub>IrCl<sub>6</sub> and Pd(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub> precursors [34]. Nevertheless, no ROCPs were formed on this catalyst, and the hydrogenation activity was found comparable to that of a reference Pd–Pt catalyst. For the selective opening of one-ring or two-ring hydrocarbons, several other combinations of noble metals have been reported: Ir–Pt [6,10,11,35], Pd–Pt [5,14], Os–Ru [5,9] Pd–Rh [13], and Pt–Rh [36]. However, a frequent limitation of the works dealing with bimetallic catalysts is the poor direct investigation of the nanoparticles structure, allowing determining whether they are themselves bimetallic or whether monometallic particles coexist [37–39].

In this article, we will show how the size and composition of ASA-supported Ir–Pd nanoparticles affect the activity–selectivity balance in high-pressure tetralin hydroconversion.

## 2. Experimental

### 2.1. Materials and catalyst preparation

Amorphous silica–alumina (ASA, commercial name SIRAL) was supplied by Sasol (Germany), following a patented preparation procedure [40,41]. SIRAL-40, containing 40 wt.% silica, was chosen as a support for its optimal performances, in correlation with its Brønsted acidity [19]. The powder, received in hydrated form, was activated by heating at 550 °C in air for 3 h. It resulted in dehydration and transformation of the alumina part from AlO(OH) (boehmite) to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. For SIRAL-40, the average oxide grain size, BET surface area, pore volume, and pore diameter were 50  $\mu$ m, 500 m<sup>2</sup> g<sup>-1</sup>, 0.90 mL g<sup>-1</sup>, and 6.4 nm, respectively. The catalysts were prepared

**Table 1**  
Metal composition of the samples, as determined by ICP-OES.

Sample name	Pd content/metal content (at.%)	Metal weight/catalyst weight (wt.%)
Ir/ASA	0	0.96
Ir89–Pd11/ASA	11	1.04
Ir55–Pd45/ASA	45	0.91
Ir11–Pd89/ASA	89	1.02
Pd/ASA	100	0.85

by incipient wetness (co-)impregnation of the supports with Ir acetylacetonate, Ir(acac)<sub>3</sub>, and/or Pd acetylacetonate, Pd(acac)<sub>2</sub>. These precursors (Sigma–Aldrich, purity 97%) were dissolved in toluene, using the concentration needed to obtain a metal loading of 1.0 wt.%. After maturation during 2 h at room temperature, the samples were dried at 120 °C overnight and reduced in an H<sub>2</sub> flow at 350–500 °C for 6 h. In the case of Ir/ASA, we have shown that the catalysts must be treated by direct H<sub>2</sub> reduction of acac-impregnated ASA, without pre-calcination, to avoid particle agglomeration [42].

The compositions of the so-called Ir(100–x)–Pd(x)/ASA sample series (x in at.%), as determined from inductively coupled plasma–optical emission spectrometry (ICP-OES, Activa – Horiba Jobin Yvon), are reported in Table 1. Prior to each activity measurement, the samples were further exposed *in situ* to an H<sub>2</sub> flow for 2 h at 350 °C.

### 2.2. Materials characterization techniques

The TG–DTA–MS (thermogravimetry–differential thermal analysis–mass spectrometry) system is described in the electronic [Supplementary material file](#).

The carbon-replicated samples were observed by high-resolution transmission electron microscopy (HRTEM). The microscopes used were Jeol 2010 (200 kV, LaB<sub>6</sub> filament, 0.19 nm resolution), 2010F (200 kV, FEG, 0.19 nm resolution), and 2100F (200 kV, FEG, Cs-corrected probe, 0.11 nm STEM resolution). They were all equipped with energy dispersive X-ray spectroscopy (EDS). Scanning TEM (STEM) was performed with the 2100F. Atomic-level high-resolution high-angle annular dark field (HAADF, Z-contrast) and bright field images were recorded.

Size histograms were obtained from the statistical treatment of the micrographs, by analyzing more than 300 particles. The metal particle size was averaged over the metal surface distribution  $n_i d_i^2$ , which is more relevant to catalysis than the number distribution  $n_i$  ( $n_i$  is the number of particles in the diameter range  $d_i$ ). The “surface-weighted mean size”  $\langle d \rangle_{surf}$  is given by  $\sum n_i d_i^3 / \sum n_i d_i^2$ .

### 2.3. Catalytic testing and product identification

The experiments were carried out in a gas-phase flow fixed bed catalytic microreactor described in details elsewhere [16]. The standard reaction conditions for tetralin hydroconversion were H<sub>2</sub> 4 MPa, tetralin 6 kPa, and 350 °C. The H<sub>2</sub>S concentration was varied between 0 and 200 ppm. The catalyst weight and the mass flow rate were adjusted for conversion control (contact time range 2–20 s).

For the catalytic tests at fixed tetralin conversion (48–56%), the catalyst weight was varied (50, 40, 20, 10, and 7 mg for increasing Pd contents), while the total flow rate was kept in the range 160–200 mL min<sup>-1</sup>, and the H<sub>2</sub>S concentration was 100 ppm.

The gas composition at the reactor outlet was determined by on-line gas sampling and gas chromatography (GC). The GC-FID was a HP 5890 II equipped with a HP-1 column (25 m × 0.2 mm × 0.5  $\mu$ m). In a typical catalytic test, at least 50 isomers of C<sub>10</sub> aromatic and saturated compounds are formed and can hardly be separated

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